

# PATENT ABSTRACTS OF JAPAN

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## (54) PRODUCTION OF LOW-MOLECULAR-WEIGHT BROMINATED POLYSTYRENE

### (57)Abstract:

**PURPOSE:** To obtain a low-molecular-weight brominated polystyrene having a low softening point and improved in compatibility with the compounded resin, flow during processing, thermal discoloration resistance and electrical properties by solution-polymerizing a brominated styrene in the presence of a chain transfer agent.

**CONSTITUTION:** A brominated styrene having a degree of nuclear substitution with bromine of 1.5-3.5 in an amount of 100 pts.wt., 1-50 pts.wt. chain transfer agent being a 3-20 C alkyl mercaptan or an  $\alpha$ -methyl-styrene dimer, 50-1000 pts. wt. organic solvent and 0.1-3.0 pts.wt. radical polymerization initiator are fed into a reactor and solution-polymerized at 50-150°C for 1-30hr. After the polymerization, a solvent serving as a poor solvent for the polymer is introduced into the reaction mixture to effect precipitation, or the solvent used in the polymerization and unreacted monomer are distilled off from the reaction mixture to obtain a low-molecular-weight brominated polystyrene having a number- average molecular weight (in terms of the polystyrene) of 1000-10000 and a softening point of 60-250°C.

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## CLAIMS

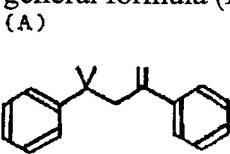
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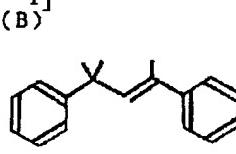
## [Claim(s)]

[Claim 1] The weight average molecular weight of the polystyrene conversion characterized by carrying out the solution polymerization of the bromination styrene to the bottom of coexistence of a chain transfer agent is the manufacture approach of the bromination polystyrene low-molecular-weight object of 1,000-10,000.

[Claim 2] The manufacture approach according to claim 1 characterized by the chain transfer agent to be used being alkyl mercaptan of carbon numbers 3-20.

[Claim 3] The alpha-methyl-styrene dimer to which the chain transfer agent to be used is expressed with the following general formula (I) [\*\* 1]

(A) 

(B) 

(I)

The manufacture approach according to claim 1 which comes out and is characterized by a certain thing.

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[0023] As a radical initiator used by the approach of this invention, azo system initiators, such as peroxide system initiator [, such as benzoyl peroxide and dicumyl peroxide, ], azobisisobutyronitril, 1, and 1'-azobis (cyclohexane-1-carbonitrile), are suitable. 0.1 - 3.0wt% of the amount of the radical initiator to be used is suitable to a bromination styrene monomer because of improvement in the quality of a rate of reaction, conversion, and a product. Moreover, it is not economically desirable to use it exceeding 3.0wt(s)%.

[0024] Although it does not limit especially concerning reaction temperature and a pressure, it is a 50-150-degree C temperature requirement, and a reaction is possible also under reduced pressure besides the reaction in ordinary pressure, and pressurization. At less than 50 degrees C, if the fall of productivity may be caused by the remarkable fall of a reaction rate and 150 degrees C is exceeded on the other hand, the side reaction and the depolymerization reactions of a bromine from a ring, such as desorption, may occur.

[0025] Moreover, although it does not limit especially concerning reaction time, 1 - 30 hours is suitable from both sides of conversion and productivity.

[0026] After a polymerization can take up a product by the approach of distilling off the approach of supplying in a solvent which is a poor solvent and settling to a polymer, or the solvent used for the polymerization, an unreacted monomer, etc.

[0027] When making it precipitate in a poor solvent and collecting polymers, it is necessary to dissolve oligomer with a natural thing depending on a residual monomer and a chain transfer agent, and the case, and to deposit a polymer. However, since the solubility of 1000 or less molecular-weight number bromination polystyrene and these residual impurity is similar, a suitable poor solvent is chosen by the balance of yield and product purity. Moreover, also with the polymer solution concentration at the time of precipitate actuation, since yield and product purity change a lot, they require cautions. For example, when using a methanol as a poor solvent, it is desirable to make polymer concentration into 15 - 30wt%.

[0028] In addition, as a solvent which turns into a poor solvent to a polymer, aliphatic series system hydrocarbon solvents, such as ketone solvent, such as ether system solvents, such as alcoholic solvent, such as a methanol, and diethylether, and an acetone, or a hexane, etc. are mentioned.

[0029] To take the approach of distilling off a solvent, an unreacted monomer, etc., it is necessary after a polymerization reaction to set the processing temperature as 200 degrees C or less more than the melting softening temperature of a polymer, and to carry out under reduced pressure. Below in softening temperature, an unreacted monomer will not fully be able to be removed but the purity of a product will fall. Moreover, coloring may be caused if it carries out under conditions which exceed 200 degrees C. About whenever [ reduced pressure ], although there is especially no convention, it is desirable to make it 200mmHg(s). When the number of average bromination to a ring exceeds 2.5, as for softening temperature, it is desirable to exceed 200 degrees C and to collect polymers by the precipitate to the above-mentioned poor solvent in such a case.

[0030] Next, although an example explains this invention concretely, this invention is not limited only to an example. In addition, this reaction is usually performed in an agitator, a thermometer, a reflux condenser, and the reactor equipped with nitrogen installation tubing.

[0031]

[Example]

In 11. 4 opening flask equipped with example 1 stirring equipment, a thermometer, a reflux cooling pipe, and nitrogen installation tubing bromination styrene with 2.02 average bromination (5.5 mol % of mono-bromination objects --) 7.7 mol % of 86.8 mol % and Tori bromination objects of JI bromination objects 200g, Toluene 300ml, n-butyl mercaptan 2.5g, and 1.0g (azobisisobutironitoriru) of azobisisobutyronitrils were taught, the temperature up was carried out to 80 degrees C under the nitrogen-gas-atmosphere mind which introduced nitrogen continuously in the reactor, and the polymerization reaction was performed for 8 hours. The conversion at this time was 92.3%. It was dropped having carried out additional dilution of the toluene 480ml at reaction mixture, and stirring in 3l. of methanols, after lowering the temperature to a room temperature. the generated precipitate -- a glass filter top -- filtration recovery -- carrying out -- 100 degrees C -- 4-hour ordinary pressure desiccation -- and similarly the vacuum drying was carried out at 100 degrees C for 4 hours, the solvent was removed, and the polymer was obtained. The yield of the obtained polymer, the weight average molecular weight of polystyrene conversion, the amount of residual monomers, softening temperature, heat-resistant coloring nature, the decrease of heating weight, Br, and S content are shown in Table 1.

[0032]

[Table 1]

	收率 (%)	ポリマー純度 (%)	分子量		軟化点 (°C)	加熱重量減少温度 (°C) 2)		耐熱着色性 <sup>3)</sup> (ガードナー色数)	元素含量	
			M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>		5%	10%		B r (%)	S (%)
実施例1	87.7	98.4	5,200	1.69	155	338	357	393	3(淡黄色)	5.9. 5 0. 4
実施例2	88.6	97.5	1,900	1.59	105	329	351	392	4(黄色)	5.8. 0 1. 1
実施例3	92.8	96.8	5,100	1.94	150	338	356	390	5(黄色)	5.7. 0
実施例4	91.9	98.2	6,300	1.57	160	339	357	392	3(淡黄色)	5.9. 3 0. 4
実施例5	85.3	97.7	4,500	2.80	160	310	344	389	12(褐色)	6.2. 0
実施例6	92.8	97.8	7,200	1.61	210	341	360	393	3(淡黄色)	6.8. 3 0. 3
比較例1	92.0	98.5	45,000	2.03	215	342	362	392	3(淡黄色)	5.9. 8
比較例2	88.9	98.1	13,000	2.23	185	343	362	393	6(淡黄色)	5.8. 8
比較例3	90.7	97.3	20,000	2.10	235	343	362	393	5(黄色)	6.8. 5
比較例4			1,000	1.68	170	318	345	393	>18(黒色)	6.8. 5

1) ポリマー純度：100%から残存モノマー、溶媒、その他低分子量体等の不純物の割合を差し引いた値。  
(ゲルパーキュロマトグラフィーの面積%により算出。)

2) 測定条件：空気中、昇温速度 10°C/min  
3) 測定方法：空気中、220°Cで1時間ポリマーを加熱した後室温まで降温し、ポリマーと同重量のジオキサンを加え溶解させその溶解色を  
ガードナー色数で表した。

[0033] The polymerization reaction was performed like the example 1 except having used 10.0g of 2n-butyl mercaptans of examples. Conversion was 92.0%. Toluene 200ml after a polymerization reaction was added, it was dropped into 2l. of methanols, and precipitate was made to generate. after filtration -- 80 degrees C -- 6-hour ordinary pressure desiccation -- similarly the vacuum drying was carried out at 80 degrees C for 4 hours, and the polymer was obtained. The yield, the molecular weight, the amount of residual monomers, many physical properties, Br, and S content of the obtained polymer are shown according to Table 1.

[0034] 200g, toluene 300ml, alpha-methyl-styrene dimersg [ 20.0 ] and 1, and 1'-azobis (cyclohexane-1-carbonitrile) (V-40, Wako Pure Chem make) 2.0g was taught for the bromination styrene of example 3 example 1, and 110 degrees

C and a 8-hour reaction were performed under nitrogen-gas-atmosphere mind. The conversion at this time was 94.1%. After the reaction, after treatment was performed by the same approach as an example 1, and the polymer was obtained. The description of yield and a product is shown according to Table 1.

[0035] The polymer was obtained like the example 1 except using 5.0g for n-dodecyl mercaptan instead of 4n-butyl mercaptan of examples. Conversion was 93.2%. The description of yield and a product is shown according to Table 1.

[0036] Except using 10.0g of carbon tetrabromide instead of 5n-butyl mercaptan of examples, the polymerization reaction was performed like the example 1 and the polymer was obtained. Conversion was 90.6%. The description of yield and a product is shown according to Table 1.

[0037] The polymer was obtained like the example 1 except using 2.5g for bromination styrene (2.9 mol % of 90.8 mol % and tetra-bromination objects of 6.3 mol % and Tori bromination objects of JI bromination objects) 200g with 2.97 example 6 average bromination, toluene 400ml, azobisisobutironitoriru1.0g, and n-butyl mercaptan. Conversion was 93.7%. The description of yield and a product is shown according to Table 1.

[0038] Using the reactor in example of comparison 1 example 1, 300g, toluene 350ml, and 3.0g of azobisisobutironitoriru were taught, the temperature up of the bromination styrene with 2.02 average bromination (7.7 mol % of 86.8 mol % and Tori bromination objects of mono-bromination objects of 5.5 mol % and JI bromination objects) was carried out to 70 degrees C under nitrogen-gas-atmosphere mind, and the polymerization reaction was performed for 6 hours. Conversion was 92.0%. Toluene 250ml was added to the reaction mixture after a temperature fall, it was dropped into 4l. of methanols of a stirring condition, and precipitate was obtained. Filtration recovered this product, the vacuum drying was carried out at 100 degrees C ordinary pressure desiccation and after that by 100 degrees C for 4 hours for 4 hours, and the polymer was obtained. The description of yield and a product is shown according to Table 1.

[0039] 200g, toluene 500ml, and 6.0g of azobisisobutironitoriru were taught, the temperature up of the bromination styrene used in the example 1 of example of comparison 2 comparison was carried out to 80 degrees C under nitrogen-gas-atmosphere mind, and the polymerization reaction was performed for 8 hours. Conversion was 93.1%. It processed like the example 1 after a reaction of a comparison, and the polymer was obtained. The description of yield and a product is shown according to Table 1.

[0040] The polymerization reaction was performed on the same conditions as the example 1 of a comparison except having used bromination styrene with 2.97 average bromination of example of comparison 3 example 5. Conversion was 91.7%. The description of yield and a product is shown according to Table 1.

[0041] Example 4 of a comparison The molecular weight of the bromination object of polystyrene with which bromination object marketing of the polystyrene is carried out, softening temperature, heating weight reduction, heat-resistant coloring nature, and a bromine content are shown according to Table 1.

[0042] Example of reference The antimony trioxide of 1 / 4 weight sections was kneaded at 200 degrees C to the bromination polystyrene and the flame retarder of the specified quantity which were prepared in an example 1, the example 2, the example 6, the example 1 of a comparison, and the example 2 of a comparison to the high-impact-polystyrene (HIPS) 100 weight section of fire-resistant performance test marketing, and the test piece was created. Measurement of an oxygen index is JIS. It carried out according to K-7201. Moreover, according to the approach of the subject 94 (UL-94V) of Underwriters Laboratories, it examined about fire retardancy using five test pieces to 1/32, 1/16, and the thickness of 1/8 inch, respectively. A result is shown in Table 2.

[0043]

[Table 2]

難燃剤	添加量 (PHR)	コン'カド'中 の臭素含量 (%)	酸素指数 (%)	UL-94燃焼試験		
				1/32インチ	1/16インチ	1/8インチ
-	0	0	18.5	HB	HB	HB
実施例1	10	5.3	21.5	V-2	V-2	V-2
	20	9.5	24.2	V-2	V-2	V-0
	30	13.0	27.5	V-0	V-0	V-0
実施例2	10	5.2	21.3	HB	V-2	V-2
	20	9.3	23.9	V-2	V-2	V-2
	30	12.7	27.2	V-0	V-0	V-0
実施例6	10	6.1	22.9	HB	V-2	V-2
	20	10.9	27.4	V-0	V-0	V-0
	30	14.9	30.7	V-0	V-0	V-0
比較例1	10	5.3	21.0	HB	HB	HB
	20	9.6	23.1	HB	V-2	V-2
	30	13.0	26.3	V-2	V-0	V-0
参考例	10	6.1	22.4	HB	V-2	V-2
	20	10.9	26.8	V-0	V-0	V-0
	30	14.9	30.0	V-0	V-0	V-0

## [0044]

[Effect of the Invention] It became possible to obtain the bromination polystyrene of the weight average molecular weight 1,000-10,000 which used bromination styrene as the raw material by this invention. Since the isolation bromine seen when polystyrene is brominated is not included, white is presented and it excels in heat-resistant coloring nature, and the electrical property at the time of blending with resin as a flame retarder further etc. becomes good. Moreover, softening temperature's weight average molecular weight is low compared with 10,000 or more bromination polystyrene quantity molecular weight objects, and compatibility with combination resin and the fluidity at the time of processing are improved.

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